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Use of immersion tin and tin alloys as a bonding medium for multilayer circuits.

(67)

A novel immersion tin composition is disclosed containing both thiourea compounds and urea compounds. A method for improving the adhesion of printed circuit boards to one another in a multilayer board and for minimizing or eliminating smear in a multilayer board is also disclosed comprising coating the metal layers of the individual circuit boards with an immersion tin coating prior to laminating them to form a multilayer board. The immersion tin composition may also be prepared from a two component system which eliminates or substantially retards the formation of H₂S in the presence of sulfur containing components.

EP 0 216 531 A1

USE OF IMMERSION TIN AND TIN ALLOYS
AS A BONDING MEDIUM FOR MULTILAYER CIRCUITS

1 1. Cross Reference to Related Patent Applications

This patent application is a continuation of U.S. Patent Application Serial No. 770,842 filed August 29, 1985.

DESCRIPTION

5 2. Technical Field

The field of the invention is printed circuit boards and a method for improving the manufacture of such boards by employing a tin immersion coating. Improved adhesion of laminae in a multilayer board, better through
10 hole plating and substantial elimination of smear are obtained by employing an immersion tin coating. A novel immersion tin coating is also disclosed.

3. Prior Art

Methods for improving the adhesion of metallic
15 layers to non-conducting surfaces of printed circuit boards in a multilayer board are disclosed by Luce, et al., in United States Patent 3,585,010; Berdan, et al., United States Patent 4,260,449 and Torday, et al., United States Patent 4,469,567. Luce, et al., disclose the production of circuit
20 board laminates employing a copper foil conductor treated by electrodepositing a thin metal layer on it. The metal consists of indium, zinc, tin, nickel, cobalt, brass, or bronze. These metals optionally may be deposited on the surface of the copper by vapor deposition.

25 Immersion tin coatings are disclosed by Orio, et al., British Patent 2,072,709; Shipley, et al., United States Patent 3,303,029 and the various references cited in Orio, et al., and Shipley, et al.

Summary of the Invention

30 The present invention relates to a novel immersion tin composition comprising:

- (a) a thiourea compound
- (b) a urea compound
- (c) a chelating agent
- 35 (d) a reducing agent
- (e) an acid and
- (f) a tin salt

1 The invention also relates to a process for
improving the adhesion of a metal layer of a printed circuit
board to the non-conductive surface of a circuit board
comprising coating the metal layer with an immersion tin
5 composition especially the composition of the invention. By
eliminating the black copper oxide layers of the prior art as
an adhesion promoting layer, better through hole plating is
realized.

By coating the metal layers of a multi layer
10 circuit board with an immersion tin composition prior to
drilling through holes in the board, smear in the holes is
eliminated or substantially eliminated thereby minimizing or
eliminating the etch-back treatment of the through-hole.
Although the inventors do not wish to be limited by any
15 theory, it is believed that the tin acts as a lubricant and
to dissipate heat during the drilling of the holes. The
composition of the invention is especially useful for this
purpose.

Detailed Description

20 The present invention relates to a novel immersion
tin composition and its use in the manufacture of printed
circuit boards. Printed circuit boards (PCB's) comprise a
non-conducting or dielectric base made up of a fibrous
material such as glass fibers, paper and the like,
25 impregnated with a resinous material such as an epoxy or
phenolic resin. The board is clad with a metal conductive
layer such as copper on either one or both surfaces.
Multilayer boards (MLB's) comprise several circuit boards
laminated to one another by means of an adhesive. In
30 addition to rigid boards (as described above), flexible
boards can be produced employing thermoplastic dielectric
layers such as fluorocarbon polymers, Nylon polymers,

1 polyimides, polyparabanic acids, and polyesters. Production
of these types of printed circuit boards are described in
Printed Circuits Handbook, Second Edition, edited by C. F.
Coombs, Jr. McGraw-Hill, 1979, which is incorporated herein
5 by reference. Laminated combinations of flexible and rigid
boards are also finding utility in some more recent
applications for MLB's. The present invention applies to all
of these structures.

10 In the manufacture of PCB's, a metal conductive
foil such as copper is bonded to the circuit board, although
for the purposes of the present invention any metal applied
to a non-conductive dielectric circuit board as a foil or by
electro deposition, electroless deposition.

15 Prior to laminating, the metal surface is treated
in an art known manner to produce electrically-conductive
lines (circuits) for the transfer of current between
components of an electrical circuit, the components
comprising by way of example, diodes, transistors, resistors,
20 capacitors, and the like. The circuits may be formed either
by a positive or a negative working photo resist, silkscreen
resist, or hand painted resist process followed by etching
and in some instances, electrodeposition of a metal or
metals, all of which is known in the art.

25 The circuits of the inner layers of an MLB are
formed by a print and etch process in which a positive
working photo resist is applied to the metal layer, a
positive circuit image projected onto the resist, followed by
a developing process to leave a positive resist pattern. The
30 positive resist pattern can also be formed by a negative
working photo resist through which a negative circuit image
is projected. The board is then etched after which the

1 positive resist is removed. The elements of the circuit
obtained do not have to be electrically connected to one
another. These circuits elements that are not connected are
placed on the board for subsequent connection to other boards
5 in the MLB array.

In MLB's, the circuit of one board is connected to
the circuit of one or more of the other boards in the
multilayers. This is achieved by forming pads or circular
areas of metal at a point or points on the conductive line or
10 lines of the board. The pads may also be isolated from the
conductive lines. The other board or boards that are to be
connected are similarly provided with pads and in the
laminating process the pads of the different boards are
aligned over one another.

15 In forming MLB's by laminating, a prepreg is
inserted between the surfaces of the boards that are to be
laminated after which the multiple layers are further treated
by applying heat and pressure to them. The prepreg generally
comprises a woven or non-woven layer or layers of fibers such
20 as glass, cellulose (e.g. paper), and the like, glass being
preferred. The prepreg also is impregnated with a so-called
"B-stage" resin such as an epoxy resin that has been
partially cured. Art known equivalents of epoxy resins are
also employed as adhesives such as acrylic resins (used with
25 polyimide circuit boards) or polyester resins.

The MLB is then pressed and cured with the pads of
the circuits of the different boards that are to be connected
aligned over one another. After curing, the pads of the
MLB's are drilled. The diameter of the drill is considerably
30 less than the diameter of the pad, the ratio of diameters
between the pad and the drill being 2:1 or greater so that
the overall structure comprises at a minimum a pad from one

1 board aligned over a pad from another board with a hole
passing through them. Since the hole in cross-section
ideally presents a surface of alternating layers of the pads
of the individual PCB's separated by the non-conductive base,
5 an electrically conductive element has to be employed in the
hole to form an electrical connection between the pads. This
is done by a process known in the art as through hole plating
(PTH).

PTH processes are also employed for connecting two
10 metal conductive surfaces having a single non-conductive or
dielectric board interposed between them for the formation of
a PCB. Boards of this type and the formation of through
holes in such boards are also within the scope of the present
invention and are intended to be included within the broad
15 definition of the MLB's as that term is used throughout the
specification.

Electroless copper is employed as a PTH plating
material. Standard electroless copper plating solutions
known in the art are used for this purpose. In order to
20 promote the deposition of electroless copper on a
non-conductive surface, the non-conductive surface is treated
with a stannous chloride sensitizer solution followed by a
super sensitizer solution of di-valent palladium chloride.
The stannous chloride is oxidized to stannic chloride and the
25 palladium chloride reduced to palladium metal. A preferred
method is to employ an activator comprising colloidal
palladium containing stannic tin. Stannic tin forms a
protective colloid around the metallic palladium, and the
solution implants a precious metal site on the non-conductive
30 surface for the purpose of initiating the deposition of the
copper by chemical reduction. A postactivator is then
employed, generally an acid, to solubilize the protective

1 colloid and expose the precious metal, i.e. palladium. The
subsequently applied electroless copper coating solution
contains a reducing agent such as formaldehyde, and when in
the presence of palladium reduces the cupric ions in the
5 solution to copper metal. The copper metal plates out on the
surface of the through hole, making electrical contact with
the walls of the metal pads through which the hole is
drilled. The electroless copper may have subsequent metal
coatings applied to it by electrolytic means.

10 Because the outer conductive metal layer of an MLB
is formed as part of the PTH process, a print and etch
procedure cannot be employed for forming circuits on this
layer. The etching step would remove the plating applied in
the through hole and would be self-defeating. For this
15 reason, after the PTH process is completed, a negative
circuit pattern is formed on the surface of the MLB by means
of a negative working photo resist, a positive circuit image
projected onto the resist followed by developing. This
leaves a negative photo resist circuit pattern on the board
20 with bare metal exposed corresponding to the area of the
circuit. The negative resist pattern can also be obtained by
a positive working photo resist through which a negative
circuit image is projected. The bare metal corresponding to
the circuit is then coated by electrolytic means with a
25 second metal that acts as an etch-resist. Tin lead alloys
are the most common material used in this respect. The etch
resist coating also coats the metal surface applied to the
through holes in the PTH process. The photo resist is then
removed and the board is etched resulting in the formation of
30 a circuit on the outer layer of the MLB having a tin lead
coating on the circuit as well as on the walls of the through
hole.

1 One of the difficulties encountered in the prior
art manufacture of MLB's is the low bonding strength
sometimes obtained between the prepreg and the metal surface
of a circuit board in the array of boards that make up the
5 MLB. These problems are especially prevalent when the metal
layer comprises copper. The bonding between the copper clad
board and the prepreg was improved by etching the copper with
amonium persulfate; however, only slightly improved bonding
strengths were obtained. Some improved adhesion over the
10 etching process was obtained by pumice spraying to micro-etch
the copper surface or provide cavities in the copper surface
to which the resin such as the epoxy resin of the prepreg
could be bonded to. Other mechanical processes such as
brushing similarly provided a mechanical alteration of the
15 surface of the copper to improve the bond strength.

Even better bond strengths between the copper layer
and the prepreg were obtained with a so-called black oxide
coating in which the copper surface of a PCB was treated with
a mixture of sodium hypochlorite and sodium hydroxide to
20 produce a black copper oxide. Although better bond strengths
were obtained, one of the difficulties with using this method
was that the composition of the sodium hypochlorite/sodium
hydroxide solution changed over a period of time and erratic
results were obtained such as varying thicknesses of the
25 black oxide. The formation of the black oxide coating was
time and temperature dependent and as a result the bath
employed for the development of the coating had to be closely
monitored. Additionally, prior to the formation of the black
oxide coating, the copper surface had to be prepared by
30 brushing, rinsing, and etching either with amonium persulfate
or a sulfuric acid - hydrogen peroxide mixture.

1 It was subsequently discovered that by lowering the
sodium hypochlorite/sodium hydroxide bath temperature from
90-95° C to 60-65° C some economies could be realized in
that less heat had to be supplied to the bath, but more
5 importantly the process was easier to control. By employing
temperatures of from about 60-65° C a bronze or brown
colored copper oxide layer was produced on the surface of the
copper and slightly better bond strengths were obtained.

 It was essential to control the black oxide
10 formation on the surface of the copper since if the
oxide was excessively thick, it would shear readily thereby
destroying the bond between the copper metal and the prepreg.
Additionally at the proper thickness, the black copper oxide
was not sufficiently flexible so that it could not be used in
15 a flexible MLB. Even though the brown or bronze colored
copper oxides obtained at the 60-65° C bath temperatures
were easier to control, these coatings were not without their
difficulties. Coating of this type were not readily accepted
by the purchasers of MLB's since they were mottled or uneven
20 in color and gave the appearance that the coating was not
uniform. This mottled appearance or "brown spotting" has
been described as affecting the dielectric properties of the
resin, and consequently, the overall performance of the
printed circuit (Cf. Berdan, et al., United States 4,260,449)
25 as well as a lowering of the peel strength of the copper foil
(i.e. bonding strength) to the prepreg (Cf. Torday, et al.,
supra, column 1, lines 27-35).

 Torday, et al. (supra) and Luce, et al. (supra),
describe methods for overcoming some of the difficulties
30 encountered with the bonding of the copper metal to the
prepreg by the electrodeposition or vapor deposition of
various alloys or metals to the surface of the copper prior

1 to bonding. One of the difficulties with the deposition of a
metal film on the copper is that the processes must be
closely controlled to assure that proper metal film
thicknesses will be obtained. Skilled operators and constant
5 monitoring of the composition and the conditions of
deposition are required in order to obtain uniform
thicknesses of these metals on copper.

Even with the prior art processes for treating the
copper metal surface to obtain better adhesion to the
10 prepreg, the laminating of the individual circuit boards to
form the MLB was a time consuming process. In the laminating
process, the individual PCB's assembled in an MLB are placed
in a press that is heated to 175°C. held there for about
10-15 minutes to bring the MLB array up to temperature after
15 which a pressure of 250-400 psi is applied. The MLB is held
at this temperature and this pressure for approximately 45-50
minutes after which heating is stopped and the MLB allowed to
cool for about 10-15 minutes while in the press. After this
cooling period, the pressure is released and the MLB is
20 removed from the press.

In subsequent operations after providing through
holes and PTH connectors, circuit components are placed on
the MLB and soldered to the circuits. Two types of soldering
methods are employed one of which comprises a hand soldering
25 process the other of which is an automatic soldering method
employing a wave soldering apparatus known in the art in
which the bottom of the MLB through which leads of circuit
components project are contacted for about 60 seconds with a
solder wave that is maintained at a temperature of
30 approximately 290° C. MLB's in which the various laminae are
not properly bonded to one another at the interfaces of the
copper foil and the prepreg will delaminate when exposed to
these soldering conditions.

1 Smearing is another difficulty encountered in the
manufacture of MLB's whereby the drill bit employed to form
the hole through the aligned pads in an MLB picks up
resinous material and deposits this material on the wall of
5 the hole. Since the wall of the hole contains alternating
resinous material layers and metal layers, the surface of the
metal layers that form part of the hole wall will be coated
with the resinous material thereby preventing any metallic
plating material applied to the surface of the hole wall from
10 contacting the metal layers and forming an electrically
conductive connection with it. It is believed that the
resinous material such as a B-stage epoxy resin used in the
prepreg comprises the principle material involved in the
smearing of the hole. Smearing, therefore, renders the PTH
15 process ineffective.

The problem of smearing is overcome by a process
known in the art as "etch-back" in which a strong mineral
acid such as sulfuric acid (optionally containing some
hydrofluoric acid) is used to etch away the "smear" from the
20 wall of the hole. Hydrofluoric acid is added to the sulfuric
acid to remove any glass fibers from the circuit board that
might be projecting into the hole. The glass fiber ends come
from the glass fiber battings employed in the manufacture of
the circuit boards or prepreg and are removed since they
25 cause imperfections in the surface of the metallic coating
applied by the PTH process.

One of the difficulties with the etch-back process
is that it requires very careful control in order to prevent
excessive etching of the wall of the hole. The concentration
30 and temperature of the etching solution has to be carefully
controlled and monitored as well as the length of time over
which the etching process is conducted. Again, because of
these critical conditions, skilled operators are required to
perform this process.

1 Precise control of the degree of etch-back is
critical in order to obtain an acceptable metal coating on
the wall of the through hole. In some instances in the
etch-back process, the etching solution will remove the
5 resinous layer of the MLB preferentially over the metal or
copper layers in the hole. This will result, after etching,
in the metal layers projecting slightly beyond the wall of
the hole as defined by the surface of the resinous material.
If this metal layer projection is excessive, the metal
10 coating applied to the wall of the hole by the PTH process
will be uneven and will not make proper electrical contact
with the metal layers in the hole.

 The phenomenon of the metal layer being etched at a
faster rate than the resinous layer in the hole is known as
15 "reverse etch" which in some instances presents the same type
of problem encountered where the metal layer projects to far
into the hole after etching.

 Another difficulty encountered in the prior art PTH
process is leaching, in which the black copper oxide formed
20 on the copper foil is deposited as a residue in the through
hole during the etch-back procedure. Although after the
etch-back process is completed the hole is rinsed, the
rinsing process is not effective to remove all of the black
copper oxide deposited on the wall of the hole. This causes
25 several problems, the first of which is that the black oxide
may interfere with the palladium catalyst deposited on the
wall of the hole for promoting the electroless deposition of
copper in the PTH process. Secondly, because the black oxide
is deposited on the wall as a non-adhering particulate
30 composition, it interferes with the bonding of the
electroless copper on the surface of the wall of the hole.
Thirdly, black oxide diffuses through the PTH coating
resulting in pin holes which interfere with the integrity of
the coating by providing sites for the coating to be attacked
35 when the MLB is subjected to etching after the PTH process is
completed.

1 The black oxide layer that forms part of the
surface of the wall of the through hole not only contributes
to these problems but is also etched away in the etch-back
process leaving a void in which etching solution components
5 are trapped. These components are not always removed in the
rinsing step and as a result also interfere with the PTH
metal layer applied to the through hole.

 Blow holes may also form in the PTH coating by the
different thermal co-efficients of expansion of the black
10 oxide and the glass material employed in the construction of
the circuit boards. The blow holes occur when the board is
submitted to extremes of temperature either during the
soldering operation or when the boards is in use. Extremes
in temperature are also encountered in the through hole after
15 electroless plating of copper when a second metal coating is
applied in the PTH process comprising a tin-lead layer that
acts as an etch resist. The tin-lead coating is applied
electrolytically and subsequently heated or flowed in order
to produce a tin-lead coating in the through hole having
20 greater integrity. Pin holes and blow holes in the PTH
coating can be the cause of reduced conductivity in the PTH
and are to be avoided for this reason.

 The use of immersion tin coatings for plating metal
surfaces is known. This process does not employ an electric
25 current but is based on an electro chemical displacement
reaction. The metal substrate that is to be plated generally
is more active (less noble) than the metal salt that is
dissolved in the coating composition or plating solution.
Copper may be plated by a tin solution even though copper is
30 more noble than tin when the immersion coating composition is
acidic and contains thiourea as a so-called "complexing"
agent. It has been theorized that the relative electrode

1 potentials of tin and copper are reversed under acidic
conditions. Once the metal substrate is completely coated,
it is no longer available to displace the metal ions in the
immersion coating composition.

5 Some of the limitations of the immersion coating
processes were the slow plating speeds, limited thickness of
the coating, as well as the extensive degreasing, cleaning
and oxide removal pre-coating steps that had to be employed.

The immersion coatings were also porous. The
10 problems of porosity were attempted to be overcome by greater
coating thicknesses. Additionally, high coating temperatures
(about 82-85°C.) had to be employed which in some instances
caused noxious fumes to be produced from the coating solution
and prevented the use of some low cost plastic materials of
15 construction for the plating tank.

Coating times of from 10 to 40 minutes were not
uncommon for this process. These times were employed in
order to obtain nonporous, relatively thick films on the
metal substrate. Additionally, the metal substrate such as a
20 copper substrate employed in circuit boards had to be grease
free and oxide free in order to obtain relatively thick tin
coatings of 80 millionths of an inch thick after about 40
minutes. (Cf. Shneble, Jr., U.S. Patent 3,917,486).

It is, therefore, an object of the present
25 invention to overcome these and other difficulties
encountered in the prior art.

A further object of the present invention is to
provide a composition for the treatment of the surface of
metal conductive layers of a circuit board and especially a
30 copper layer to promote the adhesion of the metal to a
non-conductive surface.

1 It is a further object of the present invention to
provide a process for improving the bond strength between the
conductive surfaces and the non-conductive or dielectric
layers of an MLB assembly.

5 It is also an object of the present invention to
provide a composition for treating the metal surfaces of a
circuit board to be employed in the fabrication of an MLB
that will significantly reduce the time and/or laminating
temperature used in forming the MLB while maintaining or
10 increasing the bond strength between the layers of an MLB.

 It is also an object of the present invention to
provide a process for treating the metal surfaces of a
circuit board to be employed in the fabrication of an MLB
that will significantly reduce the time and/or laminating
15 temperature used in forming the MLB while maintaining or
increasing the bond strength between the layers of an MLB.

 It is the further object of the present invention
to provide a novel composition for reducing or eliminating
smearing in an MLB.

20 It is the further object of the present invention
to provide a novel process for reducing or eliminating
smearing in an MLB.

 It is the further object of the present invention
to provide a novel immersion coating composition.

25 It is the further object of the present invention
to provide an adhesion promoting flexible metal coating on
the metal surface of a circuit board used in an MLB.

 It is also an object of the present invention to
provide a novel composition which may be employed in the
30 production of metal immersion coatings.

 It is also an object of the present invention to
provide an immersion coating that may be applied to a metal
surface that is oxidized or partially oxidized.

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1 It is a further object of the invention to
provide a novel immersion tin coating composition that
simultaneously cleans and coats a metal substrate to
which it is applied.

5 It is the further object of the present invention
to provide a novel metal immersion composition that
may be employed as a coating composition at room temperatures.

 It is the further object of the present invention
to provide such an immersion composition that may be
10 employed as a coating material that will deposit a
uniform, non-porous coating from about 0.08 to about
0.17 microns.

 It is also an object of the invention to
provide such a composition that will form a coating
15 in about 90 seconds.

 It is also an object of the present invention
to provide sulfur containing immersion coating component
compositions that do not generate intolerable levels
of hydrogen sulfide during the storage of the same.

20 It is also an object of the present invention
to provide tin sulfate containing immersion coating
compositions that provide significant improvements
over prior art tin chloride based immersion coating
compositions.

25 It is also an object of the present invention
to provide tin salt based immersion coating compositions
that do not precipitate out any significant levels
of tin compounds when stored at 20° for about 2 to 6 months.

 These and other objects have been achieved
30 according to the present invention which relates to an
immersion composition, especially an immersion tin composition
comprising:

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- 1 (a) a thiourea compound
(1-a) (b) a urea compound
 (c) a tin salt

The composition may optionally contain:

- 5 (d) a chelating agent
(1-b) (e) a reducing agent and
 (f) an acid

The acid is employed to maintain an acid pH which prevents or minimizes any oxidation reactions whereby the tin salt which is preferably a stannous salt could be oxidized to its higher valent form i.e., a stannic salt. Preferred compositions comprise those employing components (a) through (f) as listed above and those optionally containing (1-c) the salt of another metal (as noted herein) and (1-d) a surfactant

15 It has also been found that the aforesaid composition can be employed as a coating composition to improve the adhesion of a metal substrate of a PCB to a non-conductive surface of a circuit board and also eliminates, substantially eliminates or minimizes smearing when through holes are drilled in an MLB. Other immersion tin compositions can be employed in this aspect of the invention e.g. such as those disclosed in the U.S. Patents to Shipley, 3,303,029; Ceresa, et al., 2,891,871; Sullivan, et
20 al., 2,369,620; and Bradley, 2,282,511.

25 By employing an immersion tin composition and especially the composition of the present invention in the manufacture of an MLB, problems of pin holes and blow holes are eliminated, or substantially eliminated in the PTH coating.

30 The essential feature of the composition of the present invention is the use of the combination of a thiourea compound and a urea compound in an immersion coating. It has been found that when using this combination that bright,

35

1 uniform, non-porous thin coatings of tin or tin alloys can be
applied to a metal substrate. Tin or tin alloy coatings from
about 0.08 to about 0.17 microns are obtained that have good
solderability and are good etch-resists because they are
5 substantially non-porous.

The combination of the thiourea compound and urea
compound allow coating of metal substrates with substantially
no pre-cleaning or minimal pre-cleaning. The composition of
the invention acts as a cleaning composition to some degree
10 and in many instances can be applied directly on to a metal
substrate without pre-cleaning.

By way of example the immersion tin coating of the
invention, optionally containing a nickel salt and a
surfactant was applied to a copper surface that had a slight
15 oil film, fingerprints and areas of copper oxide without any
pre-cleaning of the copper surface or oxide removal. After
about 15 seconds, a bright, well adhered tin nickel coating
was obtained on the entire copper surface.

Thus the novel tin immersion coating comprising the
20 combination of the thiourea composition and urea composition
has been found to act as a cleaner and degreaser for the
metal substrate over which the coating is applied. Extensive
oil and/or grease removal and a scrubbing of the metal
substrate to remove metal oxides is either substantially
25 reduced or eliminated. The coating composition will deposit
a tin layer on a metal oxide surface such as copper oxide.

The immersion tin coatings of the invention have
been similarly applied to gold and aluminum metal substrates
and substantially the same results obtained. The application
30 of the coating therefor appears to be independent of the
reduction potentials of the metal substrates that are coated.

The components of the composition are present in
the following amounts on a molar basis:

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1 (a) about 10 to about 125 parts of a thiourea
compound
(b) about 10 to about 125 parts of a urea compound
(2-a) (c) about 1 to about 15 parts of a tin salt.
5 where the composition optionally contains a
chelating agent, a reducing agent and an acid, these
components are present in the following amounts on a molar
basis:

(d) about 5 to about 40 parts of a chelating agent
10 (2-b) (e) about 5 to about 110 parts of a reducing agent
(f) about 1 to about 30 parts of an acid.

The composition optionally may contain the salt of
a second metal in the following amounts, on a molar basis:

(g) about 0.2 to about 55 parts of a salt of a
15 (2-c) Group VIII metal, a Group IVA metal (with the
exception of tin) a Group IIB metal and Group IB
metal.

A surfactant (2-d) may also be added to the composition in an
amount as indicated herein.

20 In one aspect of the invention a composition is
provided comprising;

	Thiourea	10-100 g/l
	Urea	5-80 g/l
	Tartaric acid	5-80 g/l
25 (3-a)	Glucose	5-80 g/l
	H ₂ SO ₄ (36%)	2-60 ml/l
	SnSO ₄	1-30 g/l

Similarly where a combination of tin and another
metal is to be coated such as nickel the composition will
30 have the following components added to it:

	Triton X-100	0.5-10 ml/l
(3-b)	NiSO ₄	5-80 g/l.

1 In one embodiment, a coating composition is prepared comprising the following:

	Thiourea	60 g/l
	Urea	40 g/l
5	Tartaric Acid	40 g/l
	Glucose	40 g/l
	H ₂ SO ₄ (36%)	30 ml/l
(4)	SnSO ₄	20 g/l
	Triton X-100 (1) (optional)	5 ml/l
10	NiSO ₄ (optional)	40 g/l
	Water	balance

(1) non-ionic polyoxyethylene nonyl phenol surfactant.

Coating compositions containing about 60 g/l thiourea; about 40 g/l urea; about 40 g/l NiSO₄ and the balance water have been prepared and can form immersion tin coatings on a copper substrate.

The various equivalents as set forth herein for the foregoing components of formulas (1-a) through (1-d); (2-a) through (2-d); (3-a) and (3-b); and as known in the art may be substituted for such components on an equimolar basis.

Various combinations of tin and other metals may be used in the composition as soluble salts e.g. water soluble salts based on mineral acid or organic acid salts of these metals. The metals that may be used with tin include the soluble e.g. water soluble salts of a metal taken from Group VIII, Group IB, Group IIB and Group IVA (with the exception of tin) of The Periodic Table of the Elements and mixtures thereof. Thus, in addition to tin nickel, tin lead or tin mercury coatings, may be deposited by means of the immersion composition of the invention.

Additionally, other immersion compositions, useful for plating metal surfaces are prepared by substituting other soluble, e.g., water soluble metal salts for tin of formulas

1 (1-a) through (1-d); (2-a) through (2-d); (3-a) and (3-b);
and (4), these other metal salts comprising those based on
the metals of Group IVA; VB; VIB; VIIB; IB; IIB and IIIA of
the Periodic Table of the Elements; the group IVA, VIII, IB,
5 IIB and IIIA metals being preferred; and the Group IVA, VIII
and IB metals being especially preferred. As referred to in
the immediately preceding description, the Group IVA metals
are intended to include the Group IVA metals with the
exception of tin. The anions of these metal salts are the
10 same as those defined herein for the tin salts.
Additionally, the metal salts as defined above and herein are
preferably employed in their lowest oxidation states e.g.,
Sn(2); Ni(2); Hg(1); Au(1) and the like. Various
mixtures of these other metal salts may also be employed.
15 Salts of lead, mercury, silver, indium, gold and palladium are
especially suitable.

The tin coating compositions of the invention are
useful as an etch resist in lieu of eletrolytic tin lead etch
resists used in the manufacture of an MLB as described
20 herein.

The foregoing tin immersion coating provides many
advantages over the coatings employed in the prior art
especially the tin immersion coatings of the prior art.
Thinner pore free coatings are obtained i.e. coatings of
25 about 0.08 to about 0.175 microns compared to the prior art
in which 1-2 micron coatings (40-80 millionths of an inch)
are utilized to obtain pore free coatings.

The composition of the present invention will
produce coatings of from about 0.001 to about 0.175 microns
30 and especially from about 0.05 to about 0.175 microns. The
coating times will vary from any where between about 2
seconds up to 5 minutes (especially 5 seconds to about 120
seconds), suitable coatings (about 0.065 microns) being

1 obtained at about 30 seconds. The coating temperatures may
vary anywhere from about 0 to about 30°C., especially from
about 15 to about 25°C. although higher temperatures may also
be employed.

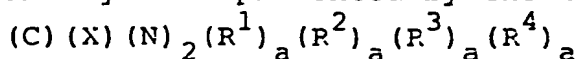
5 Excellent adhesion of the inner layers of an MLB
are obtained when the metal surfaces of the inner layers are
coated with the immersion tin coating of the present
invention prior to laminating. No delamination of an MLB
prepared in such a manner was noted after exposure of the MLB
10 to a temperature of 290°C for 10-60 seconds.

 In addition to eliminating or substantially
eliminating smearing in the through hole of an MLB, by acting
as a lubricant for the drill bit as well as a heat
dissipating material, the immersion tin coating of the
15 invention also reduces the bonding times and/or temperatures
employed in making the MLB. Typically, by coating the inner
layers of an MLB prior to laminating with the tin immersion
coating, the preheat step in the MLB laminating process may
be eliminated and the laminating time reduced to about 5 to
20 about 30 minutes from the standard 45 minute cycle ordinarily
required for this step. Pin holes and blow holes in PTH
coatings are also substantially eliminated or minimized when
employing the coating to promote adhesion of a prepreg to a
metal layer in an MLB.

25 Because the immersion tin coating layer is used in
lieu of a black copper oxide layer to promote adhesion to the
prepreg, excessive etching of the adhesion-promoting layer is
avoided with all of the problems associated with it in the
etch-back and PTH processes. The immersion tin layer is
30 substantially unaffected in an etch-back process as compared
to the black oxide layer.

1 Although various other metals may be deposited with
the tin in the novel immersion coating, it is preferred to
use a nickel salt such as nickel sulfate in the coating
composition when the coating layer is to be plated with
5 another metal. The other Group VIII metals may also be
employed in this aspect of the invention as well as the Group
IB metals IIB metals and the Group IVA metals (with the
exception of tin) and mixtures thereof.

10 The thiourea compounds and urea compounds of the
present invention may be represented by the formula:



where

$R^1 =$ (1) H

15 (2) alkyl or alkenyl having up to about 6
carbon atoms

(3) aryl, aralkyl, or alkaryl having up to
about 12 carbon atoms

(4) cycloalkyl, cycloalkylalkyl, or
alkylcycloalkyl having up to about 12 carbon atoms

20 (5) $R^5(CO)$ where R^5 may be the same as
radicals (2) through (4) as defined above for R^1

(6) CH_2OH

(7) $(C)(X)(N)_2(R^1)_a(R^2)_a(CO)_2$

(8) $(C)(X)(N)_2R^1R^2R^3$

25 (9) $(C)(X)(N)R^1R^2$

(10) $(C)(X)(N)_2R^1R^2(CO)$

R^2 , R^3 and R^4 may be the same as radicals (1)
through (6) as defined above for R^1 .

$a = 1$ or 0

30 For the thiourea compounds and their analogs
employed according to the present invention $X = S$, Se or Te ;
 X preferably is S .

1 For the urea compounds employed according to the
present invention, X = oxygen.

Mineral acid salts of the thiourea and urea
compounds may also be used.

5 The thiourea compound of the present invention
comprises either thiourea or the various art known
derivatives, homologs, or analogs thereof. Compounds that
may be employed in this respect comprise 2,4-dithiobiuret;
2,4,6-trithiotriuret; alkoxy ethers of isothiourea;
10 thiocyanuric acid (trimer of thiourea); thioammelide (trimer
of thiourea); monalkyl or dialkyl thiourea, where the alkyl
group comprises a lower alkyl group, having up to about four
carbon atoms such as diethyl thiourea or monoethyl thiourea;
saturated or unsaturated cyclic hydrocarbons mono- or
15 disubstituted thioureas such as naphthyl thiourea, diphenyl
thiourea, cyclohexyl thiourea and the like, where the cyclic
hydrocarbons has up to about ten carbon atoms; the disulfide
of thiourea; thio-imidol (the reaction product of thiourea
and sodium hydroxide); thiocarbamic acid esters (the reaction
20 products of thiourea and an alcohol comprising ROH where R
is a saturated or unsaturated aliphatic or cyclic group
having up to about ten carbon atoms) the oligomers of
thiourea and formaldehyde, e.g. monomethylol, dimethylol, and
trimethylol thioureas; S-alkyl pseudo thioureas (manufactured
25 by the reaction of thiourea with an iodo lower alkane such as
iodo methane where the lower alkyl group contains up to about
five carbon atoms); thiocarbonic acid esters of thiourea and
 R^5OH , (R^5 as defined above) especially where R^5 is lower
alkyl; thioureadioxide (aka formamidinesulfinic acid
30 [1758-73-2, C.A.Reg.No.]); the reaction product of a
saturated or unsaturated aliphatic or cyclic organic acid
having up to about 12 carbon atoms and especially the lower
aliphatic monocarboxylic acid reaction products with thiourea
e.g. acylthioureas, and the mineral acid salts of thiourea
35 e.g. thiourea mono- or di-sulfate.

1 Similarly, the urea compound comprises either urea
or the various substituted ureas or urea reaction products
such as biuret; monoalkyl or dialkyl urea, where the alkyl
group comprises a lower alkyl group having up to about four
5 carbon atoms such as diethyl urea or monoethyl urea;
saturated or unsaturated cyclic hydrocarbon mono- or
disubstituted ureas where the cyclic hydrocarbon has up to
ten carbon atoms, such as naphthyl urea, diphenyl urea,
cyclohexyl urea and the like; alkoxy ethers of iso-urea
10 especially lower alkoxy ethers of iso-urea where the lower
alkyl group contains up to about five carbon atoms, these
products being manufactured by the reaction of a lower
alkanol with cyanamide hydrochloride; acid derivatives of
urea in which the hydrogen atom of urea is substituted by an
15 acyl group, these compounds sometimes being referred to as
ureides obtained by the reaction of urea with a
monocarboxylic aliphatic saturated or unsaturated organic
acid having to about 20 carbon atoms and especially those
acids having up to about four carbon atoms; the mineral acid
20 salts of urea e.g. urea mono- or disulfate; triuret; cyanuric
acid (a trimer of urea); ammeline (a trimer of urea); imidol;
carbamic acid esters of urea and R^5OH , (where R^5 is defined
above) especially alkyl carbamates made by the reaction
product of an organic alcohol with urea especially an alkanol
25 such as a lower alkanol containing up to about four carbon
atoms; monomethylol urea, dimethylol urea, trimethylol urea
and other oligomers of urea and formaldehyde. The various
substituted ureas and their use in immersion coatings is
further disclosed by Ceresa, et al., in United States Patent
30 2,891,871 which is incorporated herein by reference.

Other urea and thiourea compounds that may be
employed comprise:

35 urea nitrate;
 urea oxalate;
 urea phosphate;
 urea sulfate;

1-acetylurea;
1-acetyl-3-methylurea;
1-acetyl-2-thiourea;
S-acetyl-2-thiourea hydrochloride;
1-allylurea;
1-allyl-3-phenylurea;
1-allyl-2-thiourea;
1-(4-aminobenzenesulfonyl)urea;
1-(4-aminobenzenesulfonyl)-2-thiourea;
1-benzoylurea;
1-benzoyl-2-thiourea;
1-benzylurea;
1-benzyl-2-thiourea;
1,3-bis(2-ethoxyphenyl)urea;
1,3-bis(4-ethoxyphenyl)urea;
1,3-bis(2-4-dinitrophenyl)urea;
1-3-bis-(hydroxymethyl)urea;
1,3-bis(1-hydroxy-2,2,2-trichloroethyl)urea;
1(2-bromo-2-ethylbutanoyl)urea;
1(2-bromo-3-methylbutanoyl)urea;
1(2-bromophenyl)urea;
1(3-bromophenyl)urea;
1(4-bromophenyl)urea;
1-butylurea;
1-sec-butylurea;
1-tert-butylurea;
1-butyl-3-phenyl-2-thiourea;
1(2-chlorophenyl)urea;
3(4-chlorophenyl)-1,1-dimethylurea;
1(2-chlorophenyl)-2-thiourea;
1(4-chlorophenyl)-2-thiourea;

- 1 1,3-diacetylurea;
1,1-diethylurea;
1,3-diethylurea;
1,3-diethyl-1,3-diphenylurea;
- 5 1,3-diethyl-1,3-diphenyl-2-thiourea;
1,3-diethyl-2-thiourea;
1,1-dimethylurea;
1,3-dimethylurea;
1,3-dimethyl-1,3-diphenylurea;
- 10 1,3-dimethyl-2-thiourea;
1,1-di(2-naphthyl)urea;
1,3-di(1-naphthyl)urea;
1,3-di(2-naphthyl)urea;
1,3-di(1-naphthyl)-2-thiourea;
- 15 1,3-di(2-naphthyl)-2-thiourea;
1,1-diphenylurea;
1,3-diphenylurea;
1,3-diphenyl-1-methylurea;
1,3-diphenyl-S-methyl-2-thiourea;
- 20 1,1-diphenyl-2-thiourea;
1,3-diphenyl-2-thiourea;
1,1-dipropyl-2-thiourea;
1,3-dipropyl-2-thiourea;
1,3-diisopropyl-2-thiourea;
- 25 1,3-di(2-tolyl)-2-thiourea;
1,3-di(4-tolyl)-2-thiourea;
1(3-ethoxyphenyl)urea;
1(4-ethoxyphenyl)urea;
1-ethylurea;
- 30 1-ethyl-1-phenylurea;
1-ethyl-3-phenylurea;
1-ethyl-3-phenyl-2-thiourea;

1 1-ethyl-2-selenourea;
1-ethyl-2-tellurourea;
1-ethylidene-2-thiourea;
1-hydroxyurea;
5 1 (hydroxymethyl) urea;
1 (2-iodo-3-methylbutanoyl) urea;
isobutylurea;
1 (2-isopropyl-4-pentenoyl) urea;
1 (4-methoxy-phenyl) urea;
10 1-methylurea;
1 (2-methyl-2-butyl) urea;
1 (3-methyl-butyl) urea;
1-methyl-3 (1-naphthyl) -2-thiourea;
1-methyl-1-nitrosourea;
15 1-methyl-3-phenyl-2-thiourea;
S-methyl-2-thiourea;
S- methylisothiouronium iodide;
S- methylisothiouronium nitrate;
S- methylisothiouronium sulfate;
20 1-methyl-2-thiourea;
1 (1-naphthyl) urea;
1 (2-naphthyl) urea;
1 (1-naphthyl) -3-phenyl-2-thiourea;
1 (1-naphthyl) -2-thiourea;
25 1 (2-naphthyl) -2-thiourea;
1-nitrourea;
1-oxalylurea;
1 (2-phenoxy-ethyl) urea;
1-phenylurea;
30 1 (phenyl-acetyl) urea;
1-phenyl-2-thiourea;
S-phenyl-2-thiourea;
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1 1-propylurea;
 2-selenourea;
 2-tellurourea;
 1(sulfonamylphenyl)urea;
5 1,1,3,3-tetraethylurea;
 1,1,3,3-tetramethylurea;
 1,1,3,3-tetramethyl-2-thiourea;
 1,1,3,3-tetraphenylurea;
 1,1,3,3-tetraphenyl-2-thiourea;
10 2-thio-1(2-tolyl)urea;
 2-thio-1(3-tolyl)urea;
 2-thio-1(4-tolyl)urea;
 2-thio-1,1,3-trimethylurea;
 2-thio-1,1,3-triphenylurea;
15 1(2-tolyl)urea;
 1(3-tolyl)urea;
 1(4-tolyl)urea;
 1,1,3-trimethylurea;

20 Some especially preferred thiourea compounds in
addition to thiourea that may be employed according to the
invention comprise:

 phenylthiourea;
 naphthylthiourea;
25 thiourea disulfide;
 oligomers of thiourea and formaldehyde;
 N-allylthiourea;

 N-mono-p-tolylthiourea (and the equivalents thereof
disclosed in U.S. Patent 4,502,927, incorporated herein by
30 reference);
 N-alkylthioureas such as methylthiourea (and the equivalents
thereof disclosed in West German Patent 3,110,478,
incorporated herein by reference);

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1 monophenylthiourea;
 metaphenylenedithiourea;
 N,N'-ethylenethiourea;
 N,N'-dibutyneylthiourea;
5 N,N'-dibutenylthiourea;
 trifluoro acetylthiourea; .
 isothiourea-S-propionic acid;
amino substituted thioureas such as thio semicarbazide and
1-phenylthiosemicarbazide;
10 1-aryl-thioureas where the aryl group is phenyl, benzyl or
naphthyl;

When substituted urea and thiourea compounds are
employed in lieu of urea and thiourea it is preferred that
each contain the same substituent. By way of example, if
15 diethylthiourea is used in the composition in lieu of
thiourea, diethylurea would be substituted for urea and so
forth.

The tin salt of the composition preferably
comprises a stannous salt. Although stannous salts of an
20 inorganic (mineral) acid or organic acid may be used
according to the invention (e.g. stannous formate, stannous
acetate and the like) the tin salt of the present invention
may comprise a stannous salt of a mineral acid such as the
sulfur, phosphorous, and halogen acids, especially the sulfur
25 acids such as sulfuric acid or sulfamic acid. Alkali metal
stannates may also be used such as sodium or potassium
stannate and the art known equivalents thereof. In one
embodiment of the invention stannous sulfate, stannous
sulfamate or stannous acetate is used as the tin salt. Where
30 tin lead coatings are deposited, lead acetate may be used as
the lead salt.

1 The acids that are employed according to the
invention may be organic acids or inorganic acids (mineral
acids) based on sulfur, phosphorous, or the halogens, the
sulfur based mineral acids being preferred such as sulfuric
5 acid or sulfamic acid. Some of the organic acids that may be
employed according to the invention comprise monocarboxylic
or dicarboxylic acids having up to about six carbon atoms
such as formic acid, acetic acid, malic acid, maleic acid,
and the like.

10 It is preferred, if possible not to use halogen
acids or halogen salts since halide residues will be produced
in the metal coating deposited, these salts interfering with
the electrical properties of the metal and may also act as
corrosive materials in the coating.

15 The chelating agents that may be employed generally
comprise the various classes of chelating agents and specific
compounds disclosed in Kirk-Othmer, Encyclopedia of Chemical
Technology, Third Edition volume 5, pages 339-368
incorporated herein by reference. Chelating agents that are
20 especially preferred comprise the aminocarboxylic acids and
the hydroxycarboxylic acids. Some specific aminocarboxylic
acids that may be employed in this respect comprise
ethylenediaminetetraacetic acid,
hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic
25 acid, N-dihydroxyethylglycine, and ethylenebis(hydroxyphenyl-
glycine). Hydroxy carboxylic acids that may be employed
comprise tartaric acid, citric acid, gluconic acid and
5-sulfosalicylic acid.

30 The various reducing agents that may be employed
according to the present invention are well known in the art
and generally comprise organic aldehydes whether saturated or
unsaturated, aliphatic or cyclic, having up to about ten
carbon atoms. Lower alkyl aldehydes having up to about six
carbon atoms may be employed in this respect such as

35

1 formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde,
and the like. Especially preferred aldehydes comprise
hydroxy aliphatic aldehydes such as glyceral-dehyde;
erythrose; threose; arabinose and the various position
5 isomers thereof and glucose and the various position isomers
thereof. Glucose has been found to act to prevent oxidation
of the metal salts to a higher oxidation state (e.g., SnII to
SnIV) but also as a chelating agent and is especially useful
for these reasons.

10 The surfactants that may be employed comprise any
non-ionic, anionic, cationic or amphoteric surfactant such as
those listed in Kirk-Othmer, Encyclopedia of Chemical
Technology, Third Edition, Volume 22, pp. 332-387 which is
incorporated herein by reference. The non-ionic surfactants
15 are especially preferred.

It has been found that where thiourea, urea, acid and
stannous sulfate are admixed together in water to
form an immersion coating solution and allowed to stand,
at 20 ± 5 °C, or at higher temperatures, hydrogen sulfide
20 forms. In order to offset this storage problem this
type of immersion coating composition is preferably
freshly made up, just prior to use, from a two part system.

Part one of such two part system would comprise
the tin salt, hypophosphorous acid and, optionally, another
25 mineral acid. The second part of such two part system
would comprise the thiourea and the urea. Where used,
the reducing agent and the chelating agent would be added
to the part containing the thiourea and urea. These two
part compositions could then each be formed as solutions
30 in about 0.5 liters of distilled water and then admixed
in approximately equal volumes to form a one liter immersion
coating solution. Immersion coating solutions of larger

1 or smaller volume can be made, obviously, by using proportionally larger or smaller volumes of each of the two precursor parts thereof.

5 A preferred part one solution could then contain
concentrated sulfuric acid 100 ml
hypophosphorous acid (50%) 40 ml
stannous sulfate 40 ml
distilled water to 0.5 liter

10 A preferred part two solution could then contain
thiourea 60 grams
urea 40 grams
distilled water to 0.5 liter

These two part compositions have H_2S off-gas levels, upon standing at $20 \pm 5^\circ C$ for ___ days, of about
15 0 to 5 ppm as compared to H_2S off gas levels of about 200 ppm for the entire tin immersion coating solution under the same conditions.

20 The hypophosphorous acid is used in these two parts compositions so as to provide, on a molar basis, about 1 to 20 especially about 1 to 10 parts of hypophosphorous acid in such part one composition and about 0.5 to 10 especially about 0.5 to 5 parts of hypophosphorous acid in the combined two part composition. The tin immersion coating compositions produced from the two component system provide minimum coating yields
25 of 150 ssf/gallon of immersion tin solution. Instron bond strengths (to Cu) obtained with measure about 4 to 5.5 lbs/inch which is comparable to that obtained with a commercially available black oxide bonding agent. (Shipley Pro Bond 80).

30 Where copper substrates as are used in multilayer circuits are immersed, at $30^\circ C$, in one liter of the above described tin immersion coating composition made from the two part precursor system, and containing hypophosphorous acid, the following coating thickness of tin were obtained
35 over the following periods of immersion time:

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1	coating time (seconds)	coating thickness (microns)
	45	0.0591
	90	0.0875
	180	0.1242
5	600	0.2839

When this same immersion bath was used at 60°C, a tin coating of 0.5914 microns was obtained on the copper substrate after 6 minutes immersion time. The levels of coated tin were ascertained by dissolving the coated tin from the Cu substrate and caculating the level of thickness based on the weight of recovered tin coating.

The following additional examples are also merely illustrative of the present invention.

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Example 1

Sulfate Versus Chloride Based Baths

Several immersion tin compositions were prepared as summarized in Table 1 below. These were either $\text{SnSO}_4/\text{H}_2\text{SO}_4$ based systems or the corresponding SnCl_2/HCl based systems. Corresponding compositions were prepared with and without urea.

Small coupons (1.5 x 0.5 inches) of copper laminate were tin coated using these immersion tin baths. The coating was done at 30°C for 90 seconds immersion using the sulfate-based baths. The coating was done at 55°C for 90 seconds immersion using the chloride-based baths. The latter baths must be operated at higher temperatures to prevent precipitation and keep all bath components in solution. Even at this higher temperature, baths 7 and 8 contained much precipitates. Coating with these baths 7 and 8 was done with the precipitate present in what appeared to be an emulsified suspension. After coating, each coupon was thoroughly rinsed in tap water and then deionized water and then air dried. The coupons were visually examined and analyzed by scanning electron microscopy (SEM) for surface morphology.

Results from the above experiment were striking. Coatings from the sulfate-based baths were shiny and uniform in appearance. Those from the chloride-based baths were dull and rather nonuniform in appearance, particularly with short immersion times. SEM analysis confirmed additional key differences. The sulfate-based coatings had a uniform coating morphology which carefully reproduced the topography of the surface. Such surface reproduction was not observed with the chloride-based coatings which were pitted and spongy.

1 Peel strengths of laminate samples prepared with
tin coatings from each of the above baths were determined.
The laminates were prepared in the following manner. A strip
(~3 x 8 inches) of 1 oz. rolled-annealed (RA) copper was
5 coated in a given bath for 90 seconds at either 30°C for the
sulfate-based baths or 55°C for the chloride-based baths.
The coated sample was rinsed thoroughly with water and air
dried. It was then used to prepare a laminate sample
consisting of the tin-coated copper strip laminated to 4
10 sheets of prepreg and a glass-epoxy baseboard. All strips
were laminated at the same time as part of a larger laminate
sample of dimensions 12 x 16 inches.

Press conditions for this lamination were:

Start at 30 tons pressure at ambient temperature.

15 Raise temperature to 345°F over 20-25 minutes.

At 345°F, raise pressure to 90 tons and temperature
to 375°F.

Keep press at 90 tons, 375°F for 45 minutes.

20 Cool to ambient temperature and then release
pressure.

Peel strengths for the peeling apart of the
tin-coated copper for the prepreg/epoxy base were measured on
an Instron unit equipped with a 90° constant angle peel test
25 accessory. Results are summarized in Table 2 below. It is
seen that peel strengths for the sulfate-based tin coatings
are significantly higher than for all of the corresponding
chloride-based coatings.

30 Use of a sulfate-based immersion tin is an
improvement over prior art based on chloride systems in that
better coatings with higher bond strengths are attainable.
Control is significantly easier and the process latitude is
wider, particularly with regard to time/temperature. Thin,
nonporous, and uniform tin coatings are possible with the
35 sulfate-based system but not with the chloride-based system.

1

TABLE 1
IMMERSION TIN BATHS

Number 1

5	Water	600 ml
	Conc. Sulfuric Acid	200 ml
	Thiourea	80 g
	Urea	40 g
	Sodium Hypophosphite	40 g
10	Stannous Sulfate	20 g
	Water	To 1 liter

Number 2

	Water	640 ml
15	Conc. Sulfuric Acid	200 ml
	Thiourea	80 ml
	Urea	0 g
	Sodium Hypophosphite	40 g
	Stannous Sulfate	20 g
20	Water	to 1 liter

Number 3

	Thiourea	60 g
25	Urea	40 g
	Tartaric Acid	30 g
	Glucose	40 g
	Conc. Sulfuric Acid	20 ml
	Stannous Sulfate	60 g
30	Triton X-100	20 g
	Water	To 1 liter

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1	Number 4	
	Thiourea	60 g
5	Urea	0 g
	Tartaric Acid	30 g
	Glucose	40 g
	Conc. Sulfuric Acid	20 ml
	Stannous Sulfate	60 g
	Triton X-100	20 g
	Water	To 1 liter
10		

15	Number 5	
	Water	507 ml
	Conc. Hydrochloric Acid	293 ml
	Thiourea	80 g
	Urea	40 g
	Sodium Hypophosphite	40 g
	Stannous Chloride (dihydrate)	21 g
20		

25	Number 6	
	Water	547 ml
	Conc. Hydrochloric Acid	293 ml
	Thiourea	80 g
	Urea	0 g
	Sodium Hypophosphite	40 g
	Stannous Chloride (dihydrate)	21 g
30		
35		

	Number 7	
1	Thiourea	60 g
	Urea	40 g
	Tartaric Acid	30 g
	Glucose	40 g
5	Conc. Hydrochloric Acid	29.3 ml
	Stannous Chloride	63 g
	(dihydrate)	
	water	to 1 liter

10	Number 8	
	Thiourea	60 g
	Urea	0 g
	Tartaric Acid	30 g
	Glucose	40 g
15	Conc. Hydrochloric Acid	29.3 ml
	Stannous Chloride	63 g
	(dihydrate)	
	Water	To 1 liter

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TABLE 2

Sulfate Versus Chloride Based Baths for Coating

Bath Number	Description	Laminate
		Peel Strength (lb/in)
1	Sulfate/hypophosphite formula with urea	4.6
2	Sulfate/hypophosphite formula without urea	4.6-4.9
3	Sulfate formula with urea	4.4
4	Sulfate formula without urea	4.0
5	Cl/hypophosphite based formula with urea	2.6
6	Cl/hypophosphite based formula w/o urea	2.6
7	Cl-based formula with urea	2
8	Cl-based formula without urea	3

Example 2

Effects of Urea/Hypophosphite In Sulfate-Based Immersion Tins

The effects of urea and hypophosphite (acid or salt) on the properties of several immersion tin compositions were examined. Results are summarized in Table 3 below. Exact compositions are provided in Table 4 below.

Tin coatings on small copper laminate coupons were prepared as in Example 1 at 30°C and 90 seconds immersion. Samples G-L of Table 3 were analyzed by EDXA and SEM.

Strips of 1 oz. copper were coated and laminated as described in Example 1 using immersion tin formulations A-D and G-L in Table 3. Peel strength measurements were made as described in Example 1.

Hydrogen sulfide off-gas levels were determined for these solutions. Each solution was allowed to equilibrate at ambient temperature overnight in a closed bottle that is half filled with immersion tin solution. Draeger tubes were used to measure the hydrogen sulfide level in each bottle upon equilibration.

Some key findings were:

Hypophosphite is effective in preventing precipitate formation.

An x-ray analysis (EDXA) of immersion tin coatings G-L showed some key effects due to the presence of urea. Coatings G-I with urea contained more tin (higher wt.% of tin) and were more pure than corresponding coatings J-L which were made without urea. Tin deposition rate with urea present was approximately 43-55% greater than without the presence of urea. Coatings made with urea present were pure while those made without the presence of urea contained substantial carbon and oxygen.

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1 Lowering the level of hypophosphite in the solution
gave lower hydrogen sulfide off-gas levels.
Hypophosphorous acid was better than sodium
hypophosphite in giving lower off-gas levels.

5 All formulations in Table 3 afforded coatings on
copper that visually, to the naked eye, appeared
uniform and shiny (on the shiny side of the 1 oz
copper coupons). This included coatings G-L which
10 were also shown essentially equivalent
morphologically as determined by SEM analysis.

The above immersion tin solutions, when partially
spent, do not behave uniformly. Formulation H, in
15 particular, afforded consistently good coatings
with continued use while quality dropped
significantly for formulations G & I. The coating
made from formulation H thus exhibited superior
longevity with use.

20 Instron bond strengths of laminates derived from
these tin coatings are consistently uniform within
experimental error and lie in the range of 3.8-5
lb/in. Such bond strengths are essentially
equivalent to the value of 4-5 lb/in that was
25 measured for a leading black oxide, Shipley Probond
80TM. All formulations appear adequate in this
regard.

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1 The above results demonstrate the utility of urea
as part of an improved immersion tin formulation for
commercial use. With urea present, fast coating rates can be
realized at ambient temperature with relatively low
hypophosphite levels. The low hypophosphite levels equate
5 low levels of hydrogen sulfide off-gas.

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Table 3

Form.	Coating	Ppt.	Peel	H ₂ S
	Amount ^a	Problem	Strength	Level
	(wt% Sn)		(lb/in)	(ppm)
A	NA	Yes	4-5	0
B	NA	Yes	4-5	0
C	NA	No	4-5	1800
D	NA	No	4-5	1900
E	NA	No	NA	600
F	NA	No	NA	300
G	21.0	No	~ 3.2	1000
H	29.4	No	~ 3.8	200
I	20.1	No	3.9	150
J	13.6	No	4.0	1200
K	19.9	No	~ 3.8	200
L	22.4	No	~ 3.85	100

a. Coating amount is equal to the weight of tin deposited per unit area (to a depth of 1 μ m for 20 kev EDXA analysis).

NA=not available, not measured.

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TABLE 4

1

Bath A

	Thiourea	60 g
	Urea	40 g
5	Tartaric Acid	30 g
	Glucose	40 g
	Conc. Sulfuric Acid	20 ml
	Stannous Sulfate	60 g
	Triton X-100	20 g
10	Water	to 1 liter

Bath B

	Thiourea	60 g
	Urea	0 g
15	Tartaric Acid	30 g
	Glucose	40 g
	Conc. Sulfuric Acid	20 ml
	Stannous Sulfate	60 g
	Triton X-100	20 g
20	Water	To 1 liter

Bath C

	Water	600 ml
	Conc. Sulfuric Acid	200 ml
25	Thiourea	80 g
	Urea	40 g
	Sodium Hypophosphite	40 g
	Stannous Sulfate	20 g
30	Water	To 1 liter

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Bath D

1	Water	640 ml
	Conc. Sulfuric Acid	200 ml
	Thiourea	80 g
	Urea	0 g
5	Sodium Hypophosphite	40 g
	Stannous Sulfate	20 g
	Water	To 1 liter

Bath E

10	Water	600 ml
	Conc. Sulfuric Acid	200 ml
	Thiourea	80 g
	Urea	20 g
	Sodium Hypophosphite	16 g
15	Stannous Sulfate	20 g
	Water	To 1 liter

Bath F

	Water	600 ml
	Conc. Sulfuric Acid	200 ml
20	Thiourea	80 g
	Urea	40 g
	Sodium Hypophosphite	5 g
	Stannous Sulfate	20 g
	Water	To 1 liter

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	Bath G	
1	Water	400 ml
	Conc. Sulfuric Acid	200 ml
	Hypophosphorus	
	Acid (50%)	20 ml
5	Thiourea	60 g
	Urea	40 g
	Stannous Sulfate	20 g
	Water	To 1 liter
10	Bath H	
	Water	500 ml
	Conc. Sulfuric Acid	100 ml
	Hypophosphorus	
	Acid (50%)	40 ml
15	Thiourea	60 g
	Urea	40 g
	Stannous Sulfate	20 g
	Water	To 1 liter
20	Bath I	
	Water	600 ml
	Conc. Sulfuric Acid	0 ml
	Hypophosphorus	
	Acid (50%)	80ml
25	Thiourea	60 g
	Urea	40 g
	Stannous Sulfate	20 g
	Water	To 1 liter
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1	Bath J	
	Water	400 ml
	Conc. Sulfuric Acid	200 ml
	Hypophosphorus	
5	Acid (50%)	20 ml
	Thiourea	60
	Urea	0 g
	Stannous Sulfate	20 g
	Water	To 1 liter
10	Bath K	
	Water	500 ml
	Conc. Sulfuric Acid	100 ml
	Hypophosphorus	
15	Acid (50%)	40 ml
	Thiourea	60 g
	Urea	0 g
	Stannous Sulfate	20 g
	Water	To 1 liter
20	Bath L	
	Water	600 ml
	Conc. Sulfuric Acid	0 ml
	Hypophosphorus	
25	Acid (50%)	80 ml
	Thiourea	60 g
	Urea	0 g
	Stannous Sulfate	20 g
	Water	To 1 liter
30		
35		

Example 3

Effects of Temperature and Immersion Time
Upon the Tin Coating

The effects of temperature and immersion time upon the tin coating were studied for two different immersion tin solutions. Four temperatures (30, 40, 50, and 60°C) and three immersion times (1.5, 3, and 6 minutes) were used. Compositions of the two immersion tin solutions are given in Table 5 below.

Coupons of copper laminate were coated under the above conditions in the manner described in Example 1. The resulting tin-coated coupons were processed as described in Example 1 and then subjected to EDXA analysis to determine the weight % tin level for each coating. Results are summarized in Table 6 below.

Visually, the coatings appeared to fall in two general classes. The coatings made with bath 1 of Table 5 at all temperatures and with bath 2 of Table 5 at low temperatures (e.g. 30°C) appeared shiny and uniform. In contrast the coatings with bath 2 of Table 5 at elevated temperatures were noticeably more dull. SEM analysis of the above coatings confirmed that the latter coatings (class 2) had different morphology. This different morphology likely arises from effects of sulfuric acid on the metal surface that are more pronounced at elevated temperatures.

Table 5

IMMERSION TIN BATHS

Bath 1

1

Water 500 ml

Conc. Sulfuric Acid 100 ml

5

Hypophosphorus

Acid (50%) 40 ml

Thiourea 60 g

Urea 40 g

Stannous Sulfate 20 g

10

Water To 1 liter

Bath 2

Hypophosphorus

Acid (50%) 80 ml

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Thiourea 60 g

Stannous Sulfate 20 g

Water To 1 liter

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Table 6
Coating Weight Percent Tin Level at Different
Temperatures and Immersion Times for Two Different Baths

5	Sample	Bath	Temp (°C)	Immersion Time (min)	Wt% Sn ^a	Instron Peel Strength (lb/inch)
10	1	1	30	1.5	26.8	4.7
	2	1	30	3.0	42.1	4.6
	3	1	30	6.0	53.9	5.0
	4	1	40	1.5	44.2	3.8
	5	1	40	3.0	54.7	4.7
	6	1	40	6.0	65.8	5.1
	7	1	50	1.5	52.7	5.1
15	8	1	50	3.0	64.1	5.3
	9	1	50	6.0	76.6	5.2
	10	1	60	1.5	58.4	2.7
	11	1	60	3.0	68.8	3.5
	12	1	60	6.0	80.1	2.7
20	13	2	30	1.5	19.0	NA
	14	2	30	3.0	21.8	NA
	15	2	30	6.0	28.9	NA
	16	2	40	1.5	27.1	NA
	17	2	40	3.0	39.0	NA
	18	2	40	6.0	49.9	NA
25	19	2	50	1.5	42.4	NA
	20	2	50	3.0	51.1	NA
	21	2	50	6.0	69.3	NA
	22	2	60	1.5	46.5	NA
30	23	2	60	3.0	59.1	NA
	24	2	60	6.0	74.1	NA

a. Wt. % Sn is equal to the weight of tin
deposited per unit area (to a depth of 1 μ m for
20 key EDXA analysis).

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NA = not available, not measured

Claims:

1. An immersion metal composition comprising:
 - (a) a thiourea compound
 - 5 (b) a urea compound
 - (c) a metal salt.
2. The composition of claim 1 further comprising:
 - 10 (d) a chelating agent
 - (e) a reducing agent
 - (f) an acid.
3. The composition of claim 1 or 2 where said
15 metal salt comprises a stannous salt.
4. The composition of claim 2 where said reducing agent comprises an aldehyde reducing agent.
- 20 5. The composition of claim 2 where said acid comprises a mineral acid and said tin salt comprises a stannous salt of a mineral acid.
6. The composition of claim 1 where said
25 thiourea compound and said urea compound comprise a thiourea nucleus and a urea nucleus with the same

substituents on each of said nuclei.

7. The composition of claim 6 where said
thiourea compound comprises thiourea and said urea
5 compound comprises urea.

8. The composition of claim 2 or 3 further
comprising a compound selected from a member of the
group consisting of a Group VIII metal salt, a Group
10 IVA metal salt with the exception of tin, a Group IIB
metal salt or a Group IB metal salt or mixtures
thereof.

9. The composition of claim 3 further comprising
15 a metal salt selected from a member of the group
consisting of the salts of iron, cobalt, and nickel or
mixtures thereof.

10. The composition of claim 9 where said salt
20 comprises a nickel salt.

11. The composition of claim 3 further comprising
a salt of lead.

25 12. The composition of claim 1 or 2 or 9 further
comprising a surfactant.

13. The composition of claim 1 or 2 or 9 further comprising a polyoxyethylene nonyl phenol surfactant.

14. The composition of claim 1 or 2 or 3 where
5 the components of said composition are present in the following amounts on a molar basis:

(a) about 10 to about 125 parts of a
thiourea compound

(b) about 10 to about 125 parts of a urea
10 compound

(c) about 1 to about 15 parts of a metal
salt.

15. The composition of claim 14 further
15 comprising the following components on a molar basis:

(d) about 5 to about 40 parts of a chelating
agent

(e) about 5 to about 110 parts of a reducing
agent

20 (f) about 1 to about 30 parts of an acid.

16. The composition of claim 14 further
comprising a compound selected from a member of the
group consisting of a Group VIII metal salt, a Group
25 IVA metal salt with the exception of tin, a Group IIB
metal salt or a Group IB metal salt or mixtures thereof

in an amount from about 0.2 parts to about 55 parts on a molar basis and said metal salt comprises a tin salt.

17. A process for improving the adhesion
5 properties of a metal layer of a circuit board to a non-conductive surface of a circuit board comprising coating said layer with an immersion tin composition.

18. The process of claim 17 where the immersion
10 composition is as claimed in any of the claims 1 to 16.

19. A process for minimizing smear in a through
hole of a printed circuit board comprising a metal
layer on a non-conductive layer comprising coating said
15 metal layer with an immersion tin composition to obtain a printed circuit board coated with said immersion tin composition; laminating at least two of said coated circuit boards to one another by means of an adhesive to obtain a laminate and drilling a through hole
20 through said laminate.

20. A process for minimizing smear as claimed in
claim 19 where the immersion composition is as claimed
in any of the claims 1 to 16.

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21. A process as claimed in claim 17 or 19 where

said metal layer comprises copper.

22. A process as claimed in claim 17 or 19 where
said printed circuit board comprises a multilayer
5 board.

23. A two component composition adapted to form
an immersion coating composition when said components
are admixed together, one of said components comprising

- 10 (a) a thiourea compound and
(b) a urea compound
and the second of said components comprising
(c) a metal salt
(d) hypophosphorous acid and
15 (e) another acid.

24. A process for forming an immersion coating
composition which comprises

- preforming two separate component
20 compositions, one of said component compositions
comprising
(a) a thiourea component and
(b) a urea compound
and the second of said components comprising
25 (c) a metal salt
(d) hypophosphorous acid and

(e) another acid
and then admixing said component compositions
together.

5 25. A composition as claimed in claim 23 or a
process as claimed in claim 24 in which (c) is a tin
salt.

10 26. A composition as claimed in claim 23 or a
process as claimed in claim 24 in which (e) is sulfuric
acid.

27. An immersion coating formed from the two
component composition of claim 23 or 25 or 26.

15

28. An immersion coating as claimed in claim 27
and further comprising

(f) a chelating agent and

(g) a reducing agent.

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29. In a process for bonding a metal to a copper
substrate in a metal immersion coating process the
improvement comprising employing as the metal immersion
coating composition in such process one as claimed in
25 claim 23.

30. In a process for bonding tin to a copper substrate in a tin immersion coating process the improvement comprising employing as the tin immersion coating composition in such process one as claimed in
5 claim 25.



European Patent
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EUROPEAN SEARCH REPORT

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Application number

DOCUMENTS CONSIDERED TO BE RELEVANT		EP 86306655.1	
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	GB - A - 2 030 781 (STANDARD TELEPHONES AND CABLES LIMITED) * Abstract; fig. 1 *	17, 19, 21	C 23 C 18/00 H 05 K 3/22
A	DE - A1 - 2 215 623 (ROBERT BOSCH GMBH) * Totality *	22, 30	
A	US - A - 4 316 322 (S.K. TRAN-BERG) * Abstract *	22, 30	
A	US - A - 4 084 022 (J. TRATZ et al.) * Abstract *	22, 30	
A	US - A - 3 875 029 (W.G. ROSEN-BERG et al.) * Claims *	1	C 23 C H 05 K
A	US - A - 3 741 905 (E.R. SAUBESTE et al.) * Abstract *	22, 30	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 17-12-1986	Examiner SLAMA
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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